

REPORT DOCUMENTATION PAGEForm Approved
OMB NO. 0704-0188

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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE Dec 20, 2003	3. REPORT TYPE AND DATES COVERED Final 10/01/99 - 06/30/03
4. TITLE AND SUBTITLE Rare Earth Doped GaN Visible and Infrared Light Emitters			5. FUNDING NUMBERS DAAD19-99-1-0348
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Cincinnati Cincinnati, OH 45221-0030			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING / MONITORING AGENCY REPORT NUMBER ASD/Research 40045-EL 8
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12 b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) The goal of this project is to investigate rare-earth-doped GaN for visible and infrared light emission applications. Our approach is to grow GaN by solid source MBE and plasma-activated nitrogen. The rare earths (such as Er, Eu, Tm, etc.) are introduced in-situ during MBE growth using Knudsen cells. We have investigated the basic materials properties of GaN:RE thin films grown on Si and sapphire substrates. Among the salient findings are the following: (1) RE incorporation is an exponential function of RE cell temperature; (2) the RE incorporation into the GaN lattice is by substitution on the Ga sites; (3) photo- and electro-luminescence reach a maximum for slightly N-rich III-V flux ratio during growth; (4) photo- and electro-luminescence reach a maximum for ~1% RE incorporation.			
14. SUBJECT TERMS GaN, MBE, rare earths, Er, Eu, Tm, light emission, electroluminescence, visible emission, infrared emission			15. NUMBER OF PAGES 11
			16. PRICE CODE
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. Z39-18
298-102

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REPORT DOCUMENTATION PAGE (SF298)
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(1) Statement of Problem Studied

Rare earth (RE) doping of GaN (and alloys with AlN and InN) has led to a new electroluminescent emission materials system at wavelengths covering the entire visible spectrum and portions of the ultraviolet and infrared spectra. GaN films doped with Eu, Er, and Tm dopants emit pure red, green, and blue (RGB) emission colors, respectively. In addition, Er-doped GaN emits strongly at 1.5 μm . As a host for RE luminescent centers, GaN possesses many properties that are ideal for bright multiple color light emission. Specifically, GaN has excellent high field transport characteristics, it is chemically and thermally rugged, and it incorporates well the RE dopants. X-ray absorption measurements have shown that even at RE dopant levels exceeding 1 at. % the majority of RE dopants occupy a strongly bonded substitutional site on the Ga sublattice. According to RE crystal field theory this tetrahedrally bonded site allows optical activation and emission from RE 4f-4f inner-shell electronic transitions. Monte Carlo calculations of GaN carrier transport have shown that at ~ 2 MV/cm applied field the average electron possesses 2.6 eV energy that is adequate for exciting blue emission. GaN:Er devices have exhibited a brightness of 500-1000 cd/m^2 at ~ 540 nm. In addition to pure colors, mixed colors can be achieved by doping with a combination of REs. For example, co-doping with Er and Tm results in an emission spectrum that is perceived by the human eye as a blue-green (turquoise) hue. Multiple color capability in a single device has also been demonstrated by adjusting the bias voltage (in a co-doped GaN:Er,Eu layer) or by switching the bias polarity (in a stacked two layer GaN:Er/GaN:Eu structure). The combination of pure or mixed color emission, the availability of bias controlled color, and the potential for white light emission indicate that GaN:RE devices have enormous potential for display applications. The strong emission at 1.5 μm from GaN:Er devices also indicates important potential for telecommunication applications.

(2) Summary of Most Important Results

As shown in Fig. 1, visible {red, green, and blue (RGB)} and infrared emission can be obtained from rare earths (REs) in-situ doped during growth into films of the III-V semiconductor GaN. Multiple color capability is a primary requirement for flat panel displays (FPDs) and agile visible and IR light sources.

This program has produced significant advances in GaN:RE science and device technology: (a) we have developed a working model for the in-situ RE doping of GaN during MBE growth; (b) we have developed GaN:RE device fabrication techniques; (c) we have developed a variety of GaN:RE thin film electroluminescent devices (ELDs).

A brief review of the GaN host properties which result in bright, multiple color capability is given in Sec. 2.1 below. GaN incorporates very well RE dopants and can provide hot carriers with average energies corresponding to excitation of blue emission, as discussed in Sec.2.2. For the GaN:RE material system the possibility of multiple color indicators which change color based solely on the polarity or magnitude of applied bias is also of great interest. In Sec. 2.3, a summary of results on voltage controlled-(VC)-ELDs and on switchable color (SC)-ELDs is presented. The VC-ELDs progress from

red to green emission with increasing bias voltage whereas the SC-ELDs switch from red to green emission based on the polarity of applied bias. Normalized red (Eu), green (Er), and blue (Tm) emission spectrums of individual GaN:RE ELDs are shown in Fig. 1. Also shown is the ~1550 nm emission from GaN:Er which is of particular interest in telecommunications applications.

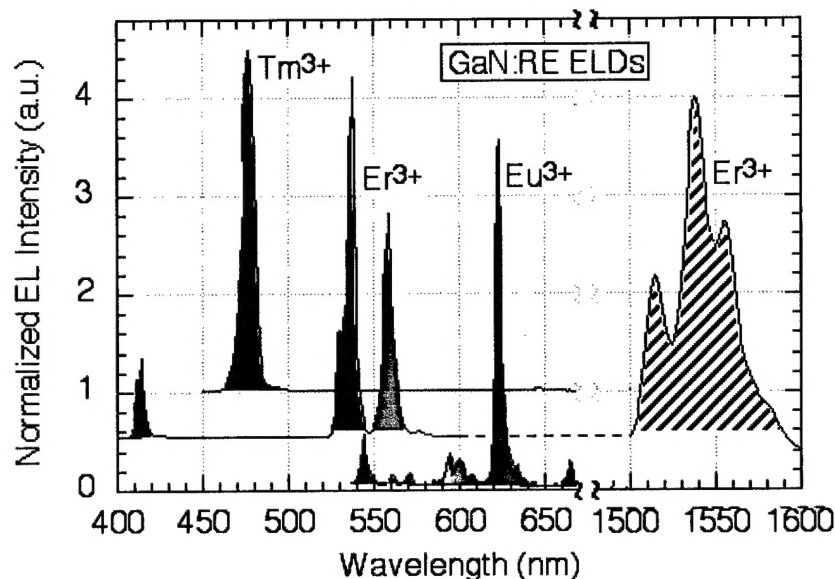
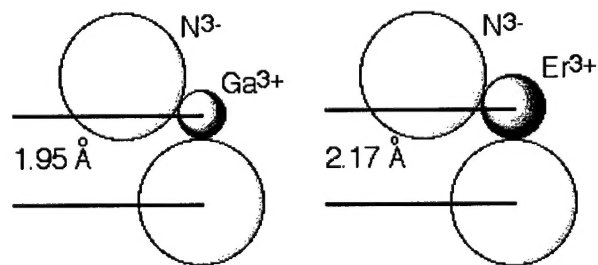


Fig. 1

The emission spectra of Tm, Er, and Eu-doped GaN ELDs showing the visible and IR wavelengths of interest. The visible peaks for each RE correspond to saturated RGB colors which can be utilized for single-, multiple-, mixed-, and full-color applications. The ~1550 nm emission from GaN:Er is of particular interest in telecommunications applications.

2.1 Rare-Earth-Doped Nitride Material system

The RE-doped GaN is grown in a Riber MBE-32 system on 2 in. p-Si (111) substrates. Ga and RE solid sources are used in conjunction with a RF plasma source supplying atomic nitrogen. For GaN:RE ELD operation indium-tin-oxide (ITO) ring contacts fabricated on the GaN:RE layer. Low voltage GaN:Er ELDs have demonstrated green emission at 5 V DC bias. High brightness GaN:Er ELDs biased with 50-100 V have exhibited a brightness as high as 500-1000 cd/m². The intense light emission from GaN:RE ELDs can be partially attributed to the ability of GaN to incorporate large concentrations of optically active RE species. In other semiconductor hosts (such as Si, GaAs), high RE concentrations result in quenching of the emission due to degradation of the host material and or RE precipitation. This ability to incorporate large RE concentrations in GaN is surprising when considering the size mismatch between RE ions and the Ga³⁺ cation, which is larger than in II-VI hosts. For comparison some relevant effective ionic radii are listed for Er-doped GaN, Si, ZnS, SrS, and AlN in the table at the right of Fig. 2.



Effective Cation Mismatch

Ga ³⁺	0.47	N ³⁻	1.44	Er ³⁺	0.78	(CN=4)
Si	1.18			Er ³⁺	1.76	(CN=10)
Zn ²⁺	0.60	S ²⁻	no data	Er ³⁺	0.78	(CN=4)
Sr ²⁺	1.18	S ²⁻	1.84	Er ³⁺	0.89	(CN=6)
Al ³⁺	0.39	N ³⁻	1.44	Er ³⁺	0.78	(CN=4)

Fig. 2 Drawing (left) indicating experimental data for the Ga-N and Er-N bond length and atomic radii in wurtzite GaN:Er. Table (right) of effective ionic radii and coordination number (CN) for Er-doped GaN, Si, ZnS, SrS, and AlN.

An X-ray absorption study of GaN:Er reveals that even at high Er concentrations (>0.1 at. %) the majority of Er ions sit substitutionally on the Ga sublattice. The experimental data for the Ga-N and Er-N bond lengths are reflected in the drawing at the left of Fig. 2.

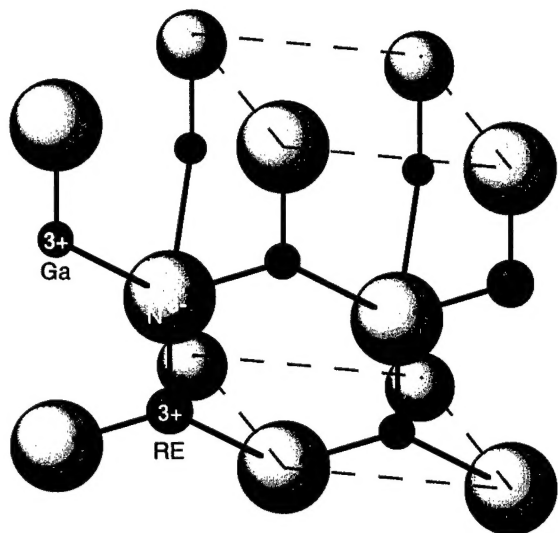


Fig. 3 Simple model of GaN:RE crystal structure showing the RE dopants on Ga sub-lattice locations.

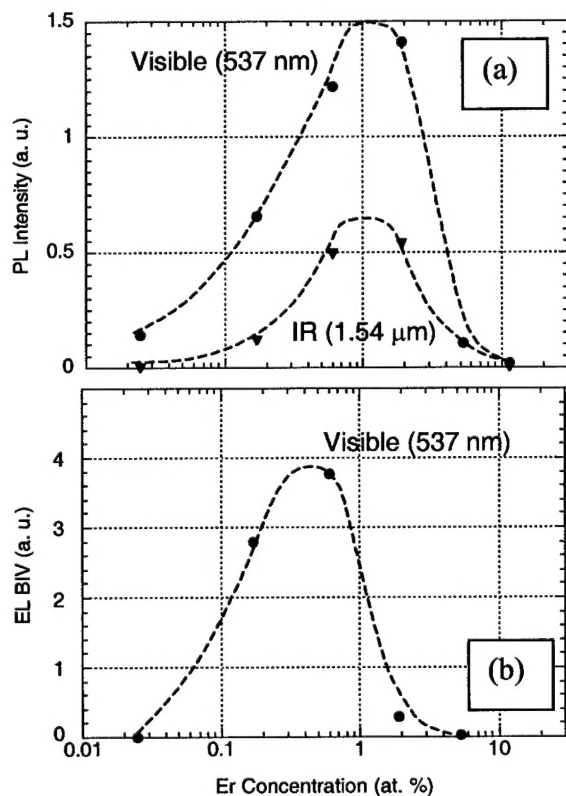


Fig. 4 PL and EL intensity vs. Er concentration: (a) visible and IR PL intensity; (b) current normalized visible EL (BIV).

In this Ga substitutional site (see Fig. 3) the tetrahedral bonding about the RE lacks inversion symmetry and results in allowance of normally forbidden RE intrashell $4f-4f$ transitions which in turn result visible light emission. GaN can incorporate RE concentration at levels comparable to or greater than that possible with commercial II-VI hosts. This is partially due to the strong bonding nature of GaN (partially covalent) compared to the more weakly bonded II-VI compounds (largely ionic). The experimentally measured Er-N bond length of 2.17 \AA is very short, a testament to its bond strength. GaN also possesses the ability to incorporate the trivalent RE ions without violating charge neutrality. Incorporating RE^{3+} in II-VI phosphors such as ZnS:Tb requires co-doping with F or O in order to satisfy charge neutrality and to achieve the best luminance and efficiency values. As shown in Fig. 4, the optimum RE dopant levels in GaN is around 1%, confirming that GaN is an excellent host for allowing large concentrations of RE dopants without severe quenching of light emission. The bonding for all RE elements is roughly similar since they all share an identical outer shell ($5s^2 5p^6$). This enables straight forward multiple color capability through co-doping GaN with several RE species. The well studied RE $4f-4f$ transitions provide several choices of RE dopant in GaN in order to create red (Eu, Pr, Sm), green (Er, Tb), blue (Tm) light and potentially white (Ho, multiple RE's) light.

2.2 Hot carrier generation

TFEL hosts such as GaN distinguish themselves from phosphors utilized in CL or PL based light emission by their high field electronic transport mechanisms. TFEL hosts need to be able to provide hot carriers with greater than 2 eV energy at an applied field of 1-2 MV/cm. This requirement has limited efficient TFEL hosts to wide band gap semiconductors.

Fig. 5 shows a qualitative plot of electron energy distribution in GaN at several applied field strengths. The pictured electron distributions are presented accurately in average energy only, as taken from Monte Carlo calculations of high field transport in GaN. The calculations show that at ~ 2 MV/cm applied field the average carrier energy is equal to that required for exciting blue (2.6 eV) emission. Also plotted in Fig. 5 is an approximate curve for the Er impact excitation cross-section of the $^2H_{11/2}$ level which results in green (~ 2.3 eV) emission. If full color capability is to be achieved in a single host, carrier energies nearing 3 eV are required. Currently, the TFEL host SrS, a II-VI compound, most efficiently provides hot carrier excitation with sufficient energy for blue emission. SrS:Cu,Ag and SrS:Ce are excellent blue and blue-green emitters but there does not exist a bright red SrS-based TFEL phosphor in order to realize full color capability in a single host. GaN:RE could potentially provide an efficient *full-color* phosphor based on a single host.

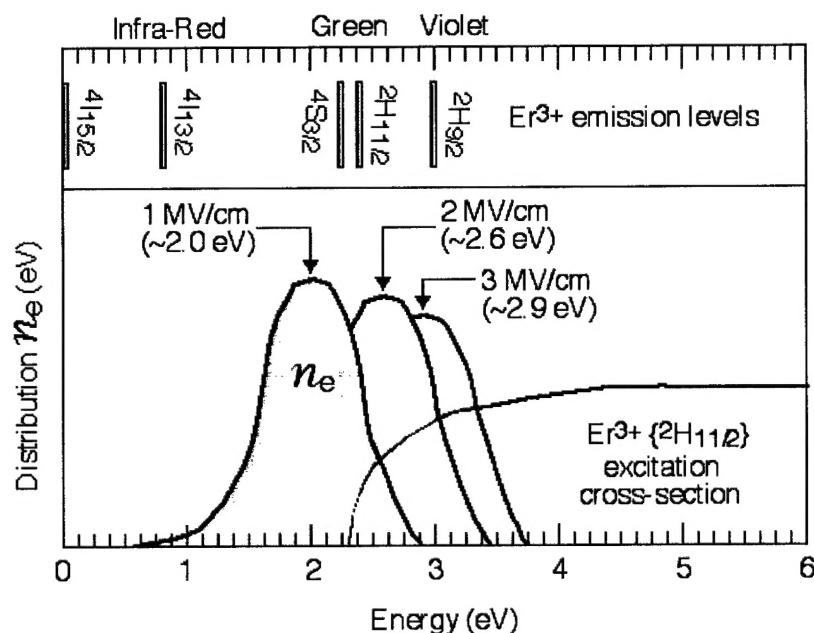


Fig. 5

Qualitative plot of electron energy distribution for 1, 2, and 3 MV/cm applied field to GaN. The pictured electron distributions are estimated based on average energy only, as determined¹² from Monte Carlo calculations of high field transport in GaN. Also shown is an approximate curve for the Er impact excitation cross-section of the $^2H_{11/2}$ which results in green (~ 2.3 eV) emission. The corresponding energy levels of dominant emissions from Er^{3+} are also shown at the top of the plot.

Carrier transport mechanisms for field strengths on the order of \sim MV/cm are not fully understood at the theoretical level. However, experimental data can be utilized to provide insight into high field transport behavior. A lanthanide (RE) doping study comparing ZnS and SrS hosts indicates that SrS is a superior material for blue TFEL. In that study the distribution of high energy carriers is obtained approximately by examining the existence and/or strength of blue and violet emission peaks compared to lower energy green, red and IR peaks. We have applied this approach to the evaluation of GaN:Er and GaN:Tm ELDs. The GaN:Er spectrum in Fig. 1 is taken at ~ 1.5 MV/cm applied field and exhibits a strong emission peak in the violet spectrum (415 nm). Referring to Fig. 5, this 415 nm peak represents a photon energy of ~ 3 eV corresponding to the $^2H_{9/2}$ Er level. This brings the qualitative plots of electron energy distribution into agreement with the observed GaN:Er spectra. For II-VI hosts the ZnS:Er spectrum saturates in the green, whereas SrS:Er has very strong violet peaks. Unlike the case of ZnS:Tm where most of the light emitted is in the IR, GaN:Tm ELDs emit a 477 nm blue emission twice as strong as the emission at 801 nm. Phosphor crystallinity can also play a major role in high field transport. For vertically biased GaN:RE ELDs fabricated with a conductive substrate as the bottom electrode, the tendency of growth in vertical columns is advantageous for high field transport since the number of grain boundaries hot carriers intercept is reduced. In summary, GaN provides adequate hot

carrier distributions for excitation of multiple color RE light emission spanning the entire visible spectrum.

2.3 Tunable and switchable-color ELDs

Given the ability of GaN:RE phosphors to emit light at multiple wavelengths some novel devices can be considered which allow bias control of the emitted color. One such TFEL device structure utilizes stacked individual color ELDs. For this style of multiple-color stacked device, the ability to independently drive 2 distinct light emitters (such as red and green) normally requires 3 electrical contacts. We have developed GaN:RE ELDs which can emit multiple colors by varying only the electrical bias on two electrodes. The first approach is based on a single GaN film co-doped with Eu and Er. The VC-ELD structure is shown in Fig. 6b. During operation, the emission from VC-ELDs can be adjusted from orange light emission (primarily Eu red, Fig 6b) to yellow emission (combination of Eu and Er green, Fig. 6a) by merely increasing the applied voltage from -70 V to -100V. The progression from orange to yellow color is likely attributed to differences in impact excitation cross-section parameters. Red emission from Eu with a long excited state lifetime (3D_0 - 7F_2 , ~1 ms) should saturate with increasing bias current before Er green emission with its shorter lifetime ($^2H_{11/2}$ - $^4I_{15/2}$, ~0.01 ms). Also, green emission (~2.3 eV) requires hotter carriers (higher applied voltage) than red emission (~2.1 eV). Other effects such as temperature quenching could also give rise to the voltage control of emission color

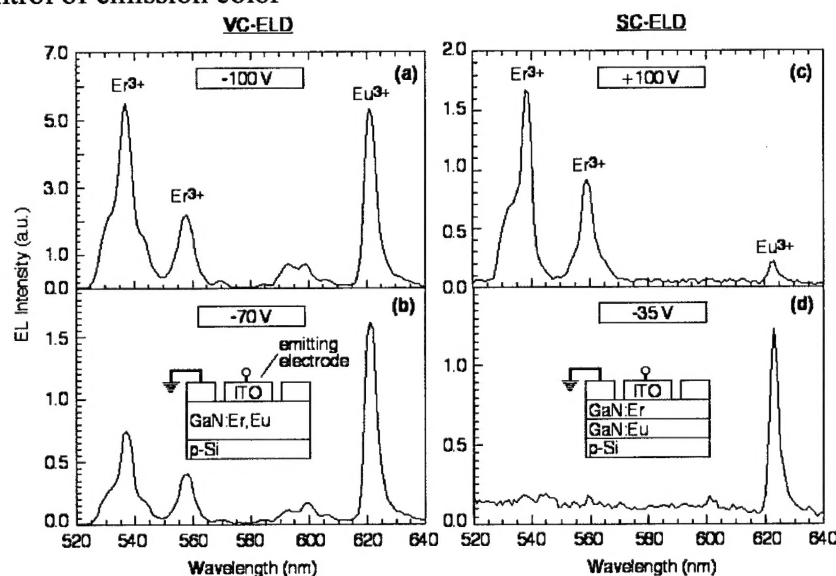


Fig. 6

(a, b) EL intensity measured from an ITO/GaN:Er,Eu/p-Si VC-ELD for -70 V (orange) and -100 V (yellow) bias applied to the emitting electrode.

(c, d) EL intensity measured from ITO/GaN:Er/GaN:Eu/p-Si SC-ELD for +100 V positive (green) and -35 V negative (red) bias applied to the emitting electrode.

SC-ELDs have also been developed utilizing the GaN:Er/GaN:Eu stacked phosphor structure shown Fig. 6d. The SC-ELDs switch from red to green emission by changing the polarity of the applied voltage: positive bias (+100 V, 0.45 mA) for saturated green emission and negative bias (-35V, -2.5 mA) for red. Some of the same underlying effects attributed to color change in VC-ELDs also likely play a role in the SC-ELDs. However, the dominant influence on color switching in SC-ELDs is attributed to polarity dependent current paths through the stacked phosphor layers. In comparison to VC-ELDs the SC-ELDs do not allow tuning of color emission but do have the advantage of a remarkable ~10X contrast between emission modes. Application of the simple SC-ELD structure to switching between other visible and/or infrared wavelengths is envisioned based on appropriate choice of RE dopants in the GaN layers.

2.4 Full color capability

One of the ultimate goals beyond multiple color capability based on GaN:RE is the prospect of full color (or white light) capability through additive light generation from integrated RGB ELDs or subtractive light generation from a codoped (GaN:Eu,Er,Tm) or stacked phosphor (GaN:Eu/GaN:Eu/GaN:Tm). Regardless of phosphor layer format, the individual GaN:RE phosphors are ideal for full color capability since the spectra are characterized by sharp dominant peaks well-matched to the definition of saturated RGB colors. This is a clear advantage for GaN:RE over many phosphors which have broad or multiple peak emission spectra which require filtering in order to generate a saturated RGB color. The full color capability of GaN:RE ELDs is illustrated using the CIE chromaticity diagram shown in Fig. 7. The triangle in the diagram connects and defines the full color capability of emission from GaN doped with Tm (blue), Er (green), and Eu (red). For comparison, commercial II-VI TFEL phosphors and CRT phosphors are incorporated into the diagram also. The II-VI TFEL and CRT phosphors provide adequate full color capability. The color triangle defined by GaN:RE phosphors encapsulates almost all of the commercialized II-VI TFEL and CRT phosphors and provides superior color capability. Based on recent successes with orange GaN:Er, Eu and turquoise GaN:Tm, Er ELDs, we expect that proper mixing of RE dopants in a GaN:Er, Eu, Tm ELD should result in white light emission. Therefore, emission of any color is envisioned possible based on TFEL of GaN doped with multiple RE dopants.

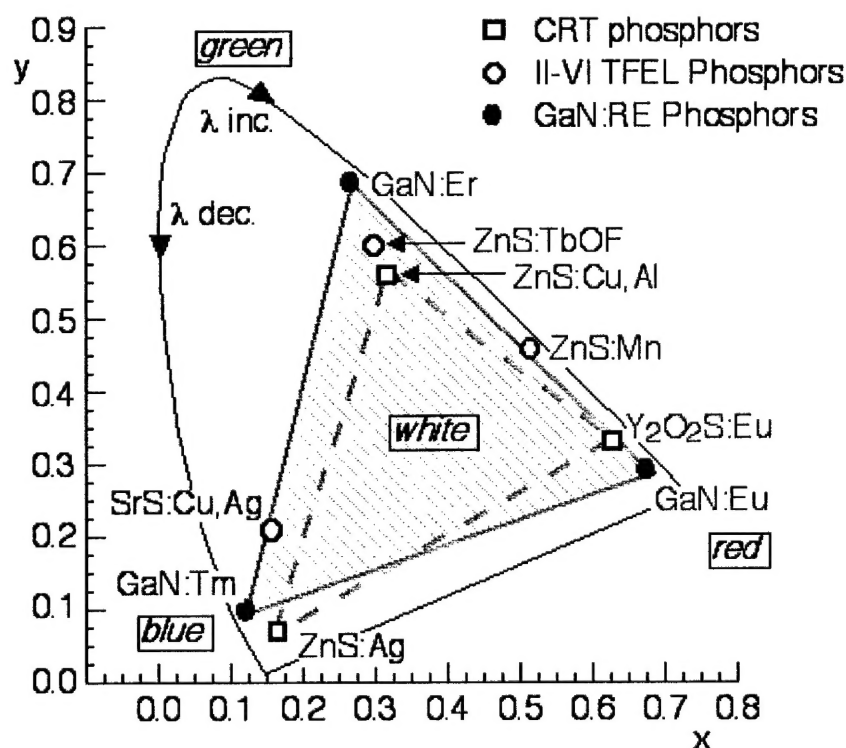


Fig. 7

CIE x-y chromaticity diagram showing the location of RGB GaN:RE ELDs (closed circles). Also shown are the coordinates of other commercial II-VI TFEL phosphors (open circles) and CRT phosphors (open squares). In addition to primary colors, mixed colors or white light can be obtained by mixing relative intensities found within the triangle defined by the individually colored constituents.

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- D. S. Lee, A. J. Steckl, E. E. Nyein, U. Hommerich, F. Pelle, and J. M. Zavada, "Enhancement of Blue Emission from Tm-Doped GaN Electroluminescent Devices", Workshop on Impurity Based Electroluminescence in Wide Bandgap Semiconductors, Santa Fe NM, April 2003.

(5) Scientific Personnel:

- Christopher Baker – **Ph. D. – 2003** - *Electroluminescent Thin Film for Integrated Optics Applications*
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- Michael Garter – **Ph. D. – 2001** - *Electroluminescent Devices Fabricated on Erbium Doped GaN*
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- Don Lee – **Ph. D. – 2002** - *Growth and Mechanisms for Rare-Earth-doped GaN Electroluminescent Devices*
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(6) Report of Inventions

- “Polarity-Controlled Color Switching Electroluminescent Devices”
Invention Disclosure: UC#99-048 – 10/25/99.
US Patent Application: Denied
- “Phosphors of Rare-Earth-Doped GaN for Thin Film Alternating Current Electroluminescent Devices”
Invention Disclosure: UC#100-062 – 10/19/00
US Patent Application: Denied
- “Electroluminescent Display Formed on Glass with a Thick Dielectric Layer”
Invention Disclosure: UC#100-065 – 11/17/00
US Patent Application: In Progress
- “Black or Color Dielectric for Electroluminescent Devices”
Invention Disclosure: UC#101-019 – 5/01/01
US Patent Application: Granted 10/21/03, Patent #6,635,306
- “Photopump Enhanced Electroluminescent Devices”
Invention Disclosure: UC#102-033 – 05/06/02
US Patent Application: In progress